

SYNTHESIS OF POLYESTERS WITH RIGID BIPHENYL SKELETON BY CARBONYLATION-POLYCONDENSATION WITH PALLADIUM-PHOSPHINE CATALYSTS

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INTRODUCTION

Stiff macromolecules are expected, when properly processed, to produce materials with high degrees of molecular orientation and order which should result in superior mechanical strength [1,2]. Biphenyl derivatives are promising components for advanced materials such as heat-resistant polymers and liquid crystalline polymers. Copolyesters based on terephthalic acid, isophthalic acid, and bisphenol A have already been used because they are heat-resistant and transparent. Wholly aromatic polyesters containing biphenyl-4,4'-dicarboxylate moiety in place of terephthalate and isophthalate moiety must be highly potential for heat-resistance. For this reason, we tried to synthesize biphenyl-containing polyesters. Among several synthetic methods, carbonylation-polycondensation method originally developed by Imai and his co-workers [3], and subsequently by Perry and his co-workers [4] on the basis of Heck reaction [5] seemed to be the most straightforward way to get target polyesters.

We report herein the successful synthesis of polyesters which contain rigid biphenyl skeleton by palladium-catalyzed carbonylation-polycondensation. Especially, introduction of 9,10-dihydrophenanthrene moieties was found to afford highly soluble polyesters in organic solvent. This is advantageous for polyester formation by carbonylation-polycondensation in solution and for molding resulting polyesters.

EXPERIMENTAL

Materials. 4,4'-Dibromobiphenyl (DBBP) and 4,4'-diiodobiphenyl (DIBP) were obtained from Aldrich Japan, Tokyo, Japan, and purified by recrystallization from toluene. 2,7-Dibromo-9,10-dihydrophenanthrene (DBDHP) and 2,7-diiodo-9,10-dihydrophenanthrene (DIDHP) were prepared from 9,10-dihydrophenanthrene by known methods [6,7]. All other materials were obtained commercially, and used with appropriate purifications.

Molecular weight measurements. The weight average molecular weight (M_w) and the number average molecular weight (M_n) were determined by means of gel permeation chromatography on the basis of a polystyrene calibration on a Yokogawa HPLC Model LC100 System (column, Tosoh TSK-Gel G4000HHR; eluent, chloroform or chloroform/1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) = 3/1 (v/v); detection, UV (wavelength: 254 nm)). Thermal characteristics were studied with a Mettler FP800 Thermal Analysis System and a MAC Science TG-DTA 2000 apparatus.

Typical procedure for carbonylation-polycondensation. In a 50 ml stainless steel autoclave equipped with a magnetic stirrer was placed 845.1 mg (2.5 mmol) of DBDHP, 570.7 mg (2.5 mmol) of bisphenol A, 17.7 mg (0.1 mmol) of $PdCl_2$, 104.9 mg (0.4 mmol) of PPH_3 , 10 ml of chlorobenzene, and 0.82 ml (5.5 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Carbon monoxide was introduced at 1.1 MPa of an initial pressure and then heated with vigorous stirring at 130 °C in an oil bath for 3 h. After excess carbon monoxide was purged, reaction mixture was poured into 100 ml of methanol. Precipitated polymer was separated from methanol by decantation, dissolved in 50 ml of chloroform, and then poured into 100 ml of methanol again with stirring. Polymer was filtered, washed with 100 ml of methanol, and dried *in vacuo* to afford poly[oxy-1,4-phenylene(1-methylethylidene)-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)-carbonyl] (**1**) as white or pale green yellow solid. The yield was 1.09 g (95%). M_w and M_w/M_n determined by GPC were 102,600 and 2.5, respectively. The 10 % weight loss temperature (T_{10}) was 414 °C and the 5 % weight loss temperature (T_5) was 394 °C in air. Found: C, 79.93; H, 5.09; Br, 1.35 %. Calcd. for $(C_{31}H_{24})_n$: C, 80.85; H, 5.25 %. IR and 1H and ^{13}C -NMR spectral data were satisfactory for polyester **1**.

The other polyesters were obtained by analogous procedures.

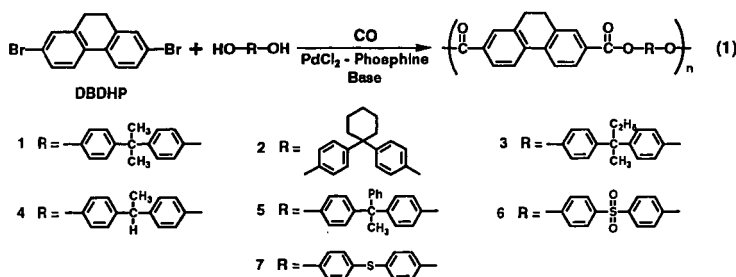
RESULTS AND DISCUSSION

Effect of reaction parameters on the carbonylation-polycondensation

The synthesis of polyesters by the carbonylation-polycondensation is shown in Eq. 1. To make clear factors controlling the synthesis, parameters such as temperature, CO pressure, solvent, and base were studied for polyester **1** from DBDHP and bisphenol A.

Figure 1 summarizes the effect of temperature on the molecular weight of **1** by the use of PPH_3 as a ligand and DBU as a base. The carbonylation-polycondensation was dependent on temperature, and the molecular weight was the highest at 120-130 °C. Low molecular weight is due to low reaction rate at low temperatures, and to side reactions at high temperatures.

Effects of solvent on the molecular weight of **1** by the use of 1,3-bis(diphenylphosphino)propane (dppp) as a ligand and DBU as a base are shown in Table 2. Although the alcoholysis of acyl-palladium intermediate is expected to be favorable in polar solvent, the solubility of product is more important factor than the polarity of solvent in our case. Polyester **1** was found to be easily dissolved in chlorobenzene, nitrobenzene, dichloromethane, and chloroform. Among them, only chlorobenzene mediated effectively the carbonylation-polycondensation. The efficiency of chlorobenzene may be due to good solubility of polyesters in it. Table 2 summarizes the effect of base on the molecular weight of **1**. The highest molecular weight was obtained for DBU. DBU was efficient under wide variety of conditions because it is a strong base ($pK_a = 11.5$). Because the salt from DBU and HBr liberated by the carbonylation was highly soluble in organic solvents, it is easier to remove HBr than the salt of other bases such as Et_3N and $i-Pr_2NEt$. Under optimum



condition, **1** was obtained in 95% yield with high molecular weight ($M_w = 1.0 \times 10^5$) as described in experimental part.

Catalytic activity of palladium-phosphine complex on the carbonylation-polycondensation is important for the molecular weight of polyesters. The effect of phosphine on the molecular weight of **1** is summarized in Table 3. The use of four moles of PPh_3 per mole of palladium was necessary to prevent catalyst decomposition, probably by a cluster formation [8]. However, large excess of PPh_3 ($\text{PPh}_3/\text{Pd} = 10$) inhibited polymer formation because excess ligands coordinated to metal center reduce the coordination of substrate and carbon monoxide. This is a different feature from the case of the ethoxycarbonylation of DBBP, where catalytic activity kept high even at high PPh_3/Pd ratio [9]. Bidentate phosphine such as dppp has been described to be more effective ligand for the carbonylation than monodentate phosphine such as PPh_3 [9-12]. In our previous work [9], high catalytic activities were observed for bidentate phosphines, α, ω -bis(diphenylphosphino)alkanes ($\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n=2-5$)), especially for dppp ($n=3$) and dppb ($n=4$) in palladium catalyzed ethoxycarbonylation of DBBP and DBDHP. The catalysts with these ligands have been much more active than those with PPh_3 . The effectiveness of bidentate ligand is due to the formation of chelated complex with palladium, such as six-membered chelate ring for dppp . In the carbonylation-polycondensation, dppp gave the highest molecular weight of **1** among them. Two fold excess of dppp for palladium was also required for the carbonylation and for high molecular weight, however, large excess of dppp prevented them. Figure 2 shows the effect of CO pressure on the molecular weight of **1** for PPh_3 and dppp . The molecular weight was the highest under CO pressure around 1 MPa, and then gradually decreased with further increase of CO pressure. Both PPh_3 and dppp were effective ligands in the carbonylation-polycondensation, especially under relatively low pressure of 0.6-1.5 MPa. However, PPh_3 was more excellent than dppp for the formation of high molecular weight polyester **1** under these conditions. The effect of CO pressure on the molecular weight of **1** for DIDHP was different from the case for DBDHP as shown in Fig. 2. The molecular weight of **1** for DIDHP was low under every pressure.

The structure of dihalide and bisphenol affected the carbonylation-polycondensation. Table 4 shows the effect of dihalide on the molecular weight of **1** by the use of dppp and DBU. Polyester **1** from DBDHP or DIDHP has higher solubility than poly[1,4-phenylene(1-methyl-ethylidene)-1,4-phenylene-carbonyl(4,4'-biphenylene-carbonyl)] (**8**) from DBBP or DIBP and accompanied the enhancement of its molecular weight. Such an increase of solubility is owing to the effect of bulkiness of 9,10-dihydrophenanthrene moiety. The molecular weight of **1** from DBDHP was higher than that from DIDHP. The difference between bromide and iodide should be explained by the difference of rate determining steps in successive reactions. Significant increase of the molecular weight of **8** was observed by the use of DIBP instead of DBBP. This was due to the enhanced reactivity of DIBP, which was compensated for negative factor of insolubility. When *p*-dibromobenzene was used as a dihalide, polyester **9** was obtained with low molecular weight due to the low solubility of the resulting polyester. Table 5 summarizes the effect of bisphenol on the molecular weight of polyesters. Bisphenols having sufficiently bulky alkyl spacers resulted moderately high molecular weight. Especially, bisphenol A gave the best results among them. Bisphenols with phenyl groups gave relatively poor results. Polyester **6** from bis(4-hydroxyphenyl)sulfone had low molecular weight. Polyester **7** from 4,4'-thiobisphenol was insoluble in the solvent. These low molecular weight is due to their low solubility.

Mechanistic aspects of the carbonylation-polycondensation

According to previous paper by Moser and his co-workers [8], active species for the carbonylation of aromatic halide is expected to be $\text{Pd}(0)\text{L}_n$ complex (L: phosphine moiety; $n: 1-4$), which is formed *in situ* from $\text{Pd}(\text{II})\text{Cl}_2$ and phosphine or from $\text{Pd}(\text{II})\text{L}_2\text{Cl}_2$ complex with phosphine. Oxidative addition of aryl halide to $\text{Pd}(0)\text{L}_n$ species, followed by CO insertion, and base mediated the alcoholysis to yield ester with regeneration of $\text{Pd}(0)\text{L}_n$. This mechanism is plausible and applicable to the carbonylation-polycondensation.

We found several characteristic features in our carbonylation-polycondensation. The molecular weight of **1** depended on the type of base. Strong organic bases such as DBU, TMEDA, and DABCO preferred to typical amines such as Et_3N and *i*-Pr₃NET. These results suggest the alcoholysis step is a key step for the increase of molecular weight. Similar effects of base were observed in the carbonylation of 4-bromobiphenyl [12]. The molecular weight of **1** for DIDHP was inferior to that for DBDHP. The effects of CO pressure on the molecular weight of **1** for DIDHP were quite different from the case for DBDHP. These results mean that the oxidative addition of halide to $\text{Pd}(0)\text{L}_n$ is not so important for the increase of the molecular weight of resulting polyesters.

Figure 3 shows time dependence curves on CO consumption by the use of dppp and PPh_3 , respectively, under atmospheric pressure. The periods, for which half amount of carbon monoxide was consumed for the reaction, were 16 min and 32 min in the case of dppp and of PPh_3 ,

respectively. This means that catalytic activity for dppp is apparently higher than that for PPh₃. Figure 4 shows time dependence on the M_w by use of dppp and PPh₃, respectively, under the same condition as in Fig. 3. Initial rate of the increase of M_w for dppp is obviously larger than that for PPh₃, whereas final M_w for PPh₃ is higher than that for dppp. These results mean that catalytic activity is not parallel to final molecular weight of resulting polyesters, and that some inhibiting reactions may occur during the growth of the polyester in the case of dppp. We should note the side reactions because the rate of polyester formation should not affect the final molecular weight of polyester. To know whether side reactions take place or not, the phenoxycarbonylation of DBBP using the catalyst with dppp or PPh₃ was examined. Diphenyl biphenyl-4,4'-dicarboxylate was observed as a sole product from DBBP in high yield in both cases. Only a detectable product except the esters from DBBP was phenyl benzoate judging from GC analysis. This product should form via the carbonylation of chlorobenzene used as a reaction solvent. Amount of phenyl benzoate was 0.115 mmol with dppp and 0.044 mmol with PPh₃, respectively, from phenol (6.0 mmol) and chlorobenzene (10 ml) in the presence of DBBP (2.5 mmol). The amount of phenyl benzoate arising during the carbonylation-polycondensation with dppp was about three times larger than that with PPh₃. It is evident that the benzoyl complex as an intermediate of the carbonylation of chlorobenzene can act as a terminator of the carbonylation-polycondensation. This is a possible reason why the molecular weight of **1** with dppp is lower than that with PPh₃ in spite of higher catalytic activity of palladium-dppp complex. These results show that in order to obtain the polyesters with high molecular weight, the selectivity of the catalyst for the carbonylation is more important factor than catalytic activity.

Thermal properties of polyesters

Wholly aromatic polyesters **1-9** did not have melting point and glass transition temperature up to 400 °C. The 10 % weight loss temperature (T_{10}) values of them were above 380 °C in air. On the basis of TG profiles, polyesters **1** and **8** were more stable than **9** at 300-390 °C, although they lost their weights faster than **9** above 400 °C. Polyesters **1** and **5** were soluble in chloroform and dichloromethane. Soluble polyesters with M_w larger than 10,000 easily formed transparent casting films.

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Table 1. Effects of solvent on the synthesis of **1**^{a)}

Run	Solvent	Yield (%)	M_w ($\times 10^3$)	(M_w/M_n)
1	Chlorobenzene	99	35	(3.6)
2	Anisole	99	25	(4.0)
3	Fluorobenzene	98	6.7	(2.3)
4	Benzene	94	5.8	(2.1)
5	Nitrobenzene	0	-	-

a) Reaction conditions: DBDHP 2.5 mmol, bisphenol A 2.5 mmol, PdCl₂ 0.1 mmol, dppp 0.2 mmol, DBU 5.5 mmol, solvent 10 ml, CO pressure 2.1 MPa, temperature 120 °C, period 3 h.

Table 2. Effects of base on the synthesis of **1**^{a)}

Run	Base	Yield (%)	M_w ($\times 10^3$)	(M_w/M_n)
6	DBU	95 ^{b)}	92	(2.5)
7	TMEDA ^{d)}	99	16	(3.3)
8	DABCO ^{c)}	96 ^{b)}	12	(4.1)
9	Et ₃ N	92 ^{b)}	4.5	(3.0)
10	<i>i</i> -Pr ₃ NEt	22	0.9	(1.4)

a) Reaction conditions: DBDHP 2.5 mmol, bisphenol A 2.5 mmol, PdCl₂ 0.1 mmol, PPh₃ 0.4 mol, DBU 5.5 mmol, chlorobenzene 10 ml, CO pressure 2.1 MPa, temperature 120 °C, period 3 h. b) dppp 0.2 mmol, was used as a ligand. c) Palladium precipitate was observed. d) *N,N,N',N'*-tetramethylethylenediamine. e) 1,4-Diazabicyclo[2.2.2]octane.

Table 3. Effects of catalyst on the synthesis of **1**^{a)}

Run	Catalyst	Yield (%)	M _w (x10 ³)	(M _w /M _n)
11	PdCl ₂ /2PPh ₃	39	1.2	(1.6)
12	PdCl ₂ /4PPh ₃	92	37	(3.0)
13	Pd(PPh ₃) ₄ ^{b)}	96	19	(3.8)
14	PdCl ₂ /2dppe ^{c)}	94	12	(3.6)
15	PdCl ₂ /dppp ^{d)}	97	6.2	(2.5)
16	PdCl ₂ /2dppp	99	35	(3.6)
17	PdCl ₂ /5dppp	39	1.2	(1.6)
18	PdCl ₂ /2dppb ^{e)}	95	21	(3.4)
19	PdCl ₂ /2dppe ^{f)}	91	17	(3.2)

a) Reaction conditions: DBDHP 2.5 mmol, bisphenol A 2.5 mmol, PdCl₂ 0.1 mmol, phosphine 0.1-0.5 mmol, DBU 5.5 mmol, chlorobenzene 10 ml, CO pressure 2.1 MPa, temperature 120 °C, period 3 h. b) Pd(PPh₃)₄, 0.1 mmol. c) 1,2-bis(diphenylphosphino)ethane. d) 1,3-bis(diphenylphosphino)propane. e) 1,4-bis(diphenylphosphino)butane. f) 1,5-bis(di-phenylphosphino)hexane.

Table 4. Polyesters of dihalides with bisphenol A^{a)}

Run	Dihalobiphenyl	Polyester	Yield (%)	M _w (x10 ³)	(M _w /M _n)
20	DBDHP	1	99	35	(3.6)
21	DIDHP	1	98	24	(2.8)
22	DBBP	8	94	5.6	(6.3)
23	DIBP	8	94	12	(2.5)
24	<i>p</i> -Dibromobenzene	9	96	2.6	(2.5)

a) Reaction conditions: dihalide 2.5 mmol, bisphenol A 2.5 mmol, PdCl₂ 0.1 mmol, dppp 0.2 mmol, DBU 5.5 mmol, chlorobenzene 10 ml, CO pressure 2.1 MPa, temperature 120 °C, period 3 h.

Table 5. Polyesters of bisphenols with DBDHP^{a)}

Run	Bisphenol	Polyester	Yield (%)	M _w (x10 ³)	(M _w /M _n)	Remarks
26	Bisphenol A	1	99	35	(3.6)	-
27	4,4'-Cyclohexylidenebisphenol	2	93	20	(3.1)	-
28	4,4'-(<i>s</i> -Butylidene)bisphenol ^{b)}	3	97	13	(3.0)	-
29	4,4'-Ethylidenebisphenol	4	98	12	(2.7)	+
30	4,4'-(1-Phenylethylidene)bisphenol	5	99	25	(3.7)	-
31	4,4'-Sulfonylbisphenol	6	77	1.2	(2.0)	++
32	4,4'-Triobisphenol	7	99	insoluble		++

a) Reaction conditions: DBDHP 2.5 mmol, bisphenol 2.5 mmol, PdCl₂ 0.1 mmol, dppp 0.4 mmol, DBU 5.5 mmol, chlorobenzene 10 ml, CO pressure 2.1 MPa, temperature 120 °C, period 3-5 h. b) CO pressure 1.1 MPa. c) Outlook of reaction mixture just after the reaction. -: homogenous. +: slightly suspended. ++: suspended.

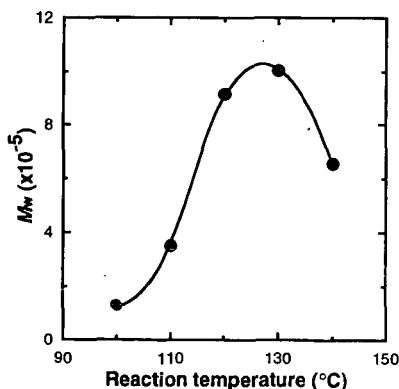


Fig. 1. Effect of reaction temperature on the molecular weight of **1**. Reaction conditions: DBDHP 2.5 mmol, bisphenol A 2.5 mmol, PdCl₂ 0.1 mmol, PPh₃ 0.2 mmol, DBU 5.5 mmol, chlorobenzene 10 ml, CO pressure 1.1 MPa, period 3 h.

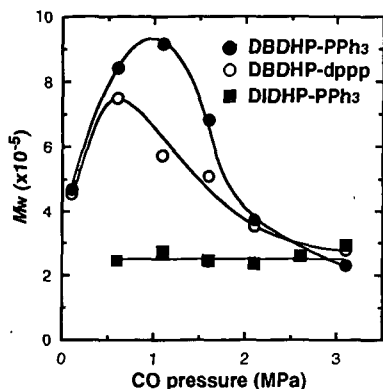


Fig. 2. Effect of CO pressure on the molecular weight of **1**. Reaction conditions: dihalide 2.5 mmol, bisphenol A 2.5 mmol, PdCl₂ 0.1 mmol, PPh₃ 0.2 mmol or dppp 0.1 mmol, DBU 5.5 mmol, chlorobenzene 10 ml, temperature 120 °C, period 3 h.

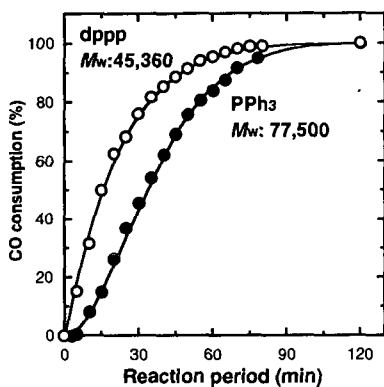


Fig. 3. CO consumption during the carbonylation-polycondensation. Reaction conditions: DBDHP 2.5 mmol, bisphenol A 2.5 mmol, PdCl₂ 0.1 mmol, PPh₃ 0.4 mmol or dppp 0.2 mmol, DBU 5.5 mmol, chlorobenzene 10 ml, CO pressure 0.1 MPa.

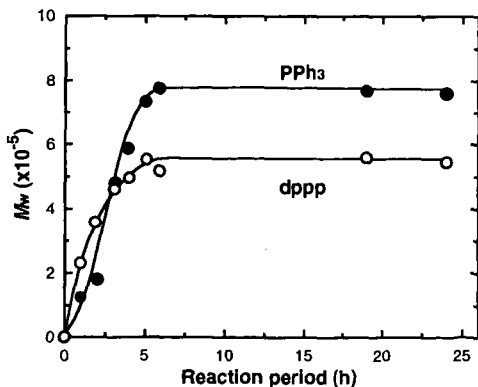


Fig. 4. Time dependence of the molecular weight on the synthesis of **1**. Reaction conditions: DBDHP 2.5 mmol, bisphenol A 2.5 mmol, PdCl₂ 0.1 mmol, PPh₃ 0.4 mmol or dppp 0.2 mmol, DBU 5.5 mmol, chlorobenzene 10 ml, CO pressure 0.1 MPa.